INORGANIC NITROGEN IN GREEN RIVER FORMATION OIL SHALE*

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ABSTRACT

    Inorganic (mineral) N has been found in both raw and retorted Green River
Formation oil shale.  Buddingtonite, an ammonium-bearing feldspar, has been
identified in some shales by X-ray diffraction, and ammonium ion ($NH_4^+$) has
been found in the same and other shales by infrared adsorption.  Measurement of
total N content of low-temperature ashed oil shale by a combustion technique is
proposed as a method of measuring inorganic-N content.  The method is based on the
observation that the N content of buddingtonite is not reduced by low temperature
ashing.  Use of this technique demonstrates that inorganic N content is variable
and is the major source of nitrogen in some oil shale samples.  The fate of both
organic and inorganic N during pyrolysis is also discussed.

INTRODUCTION

    Within the United States are large and rich deposits of oil shale.  Formost of
these is the oil shale of the Green River Formation of Colorado and Utah.  This
shale contains approximately 0.5 wt% N, but the concentration is variable, ranging
from 0.2% to as much as 1%. Pyrolysis of oil shale produces ammonia which needs to
be removed from the retort water before recycling or disposal (1).  N in shale oil
must be reduced to produce stable, non-polluting transportation fuels, and removal
of N requires special catalysts and consumes H increasing the cost of refining
(2).  Nitric oxide (NO) is produced when retorted shale is burned as a fuel (3,4).

    The ratio of N to organic C both in samples of Green River oil shale and in
kerogen isolated from the same samples has been measured but only a slightly
higher ratio in whole shale than in kerogen, was found suggesting that most of the
N (90%) is organic (5,6).  This is qualitatively consistent with the observation
by most workers that  N content of oil shale increases with an increase in grade
or organic C content (6-9).  However, correlation of organic C with N does not
prove that N is organic; N may have originated in organic debris, but has been
transferred to the inorganic matrix during diagenesis.  Finally, some of the
published data on N content as a function or organic C content show a non-zero
intercept (7-9), suggesting shale contains some N even in the absence of organic C.

    Recently, Cooper and Evans (10) utilized HF-HCl digestion in the determination
of inorganic N and concluded, in conflict with prevailing opinions, that most  N
in both raw and retorted shale was inorganic in form.  Later, Nadkarni (11) showed
that the measured "total" N content for some shales depended on the technique
used.  For a sample of Colorado shale, the Kjeldahl method measured a N
concentration of 0.45±0.05% while combustion (Dumas) methods gave a value of
0.74±0.16%.  These two papers cast doubt about the data on which the previous
conclusions have been based.

    Most of the N in the Condor oil shale deposit of Australia is inorganic.  It
is found as an ammonium silicate of the feldspar family called buddingtonite, and
the concentration of this mineral in the Condor shale is approximately 10 wt% (12).

The purpose of this report is to put proper perspective on the occurrence and abundance of inorganic N in Green River oil shale.

EXPERIMENTAL SECTION

All samples used in this investigation were ground to a talc-like consistency in a rotating concentric disk and ring (Bleuler) mill before analysis. Past experience indicates that essentially all material prepared by this procedure passes a 325 mesh sieve and most was >10μ in diameter. Some samples were treated with 1 M HCl overnight to remove carbonate minerals.

Some samples were low-temperature ashed in an oxygen plasma (LEF Corp. LTA-504) to remove organic matter. The oxygen pressure was maintained a 1 torr, and the total power in each of the four chambers was 250 watts.

Carbon, H and N content were measured at LLNL by either a Perkin-Elmer Model 240 or Leco model CHN-600 elemental analyzer. The samples size for the Perkin-Elmer instrument was 2-4 mg, and the sample size for the Leco instrument was 100 mg. To ensure good precision 3 to 4 replicates were measured for each reported value. Organic C was determined by the difference between total C and that evolved by 1 M HCl and collected on ascarite. Although the reproducibility among determinations of N concentration of a given sample at a given time was generally ±0.02 wt% N, the agreement among groups of N analyses for the same shale over a period of several years was not as good. The reasons for this are not clear. Because of this problem some samples were sent to J&A Associates, Golden, Colorado, for measurement of total N by means of an Antek Chemiluminescence Analyzer Model 707.

A Digilab Model FTS-20c infrared spectrometer was used to measure the infrared spectrum in the transmission mode. Each sample was diluted to approximately 2% in KBr and pressed into a pellet.

A Phillips Diffractometer was used to determine the x-ray powder patterns. Early patterns were recorded on strip-chart recorders, but recent patterns were recorded and processed by computer.

A sample of buddingtonite, identified as California 117751-6, was acquired from the Smithsonian Institution (13). The N content was measured at 1.69% at LLNL and 2.78% at J&A Associates.

A description of the oil shale samples used is given in Table 1. Most of them have been used in other investigations at LLNL or other laboratories. The chemical analyses are values averaged from at least 3 samples from the same batch of shale determined at different times.

RESULTS

Identification of buddingtonite in oil shale by x-ray diffraction

Buddingtonite was first discovered in oil shale (sample L-1 9A/5) by G. Smith at LLNL in 1976 as part of a routine x-ray analysis of raw shale to be used in the L-1 retorting experiment (15). Buddingtonite was also identified in raw and retorted shale (sample RI 8008-76) in an unpublished 1978 investigation on the analysis of dawsonite in oil shale.

Table 2 compares d-spacings for 10 strongest x-ray diffraction peaks of buddingtonite, based on the ASTM standard #17-517, to those from our measurements of the Smithsonian Institution (SI) sample of buddingtonite. Peaks apparently due to buddingtonite in two Colorado oil shale samples and one sample of buddingtonite

| # | I.D. | Location | Oil Yield (gpt) | Chemical Composition, Wt% | | | | | | %Inorg. N[a] |
|---|------|----------|-----------------|---|---|---|---|---|---|---|
| | | | | C | acid CO$_2$ | org. C | H | S | N | |
| 1 | Ca37 | Tract Ca | 34.3 | 21.90 | 15.98 | 17.5 | 2.38 | -- | 0.61 | 21 |
| 2 | Ca25 | Tract Ca | 24.8 | 16.57 | 19.67 | 11.2 | 1.68 | 1.1 | 0.54 | 43 |
| 3 | AP60 | Anvil Points | 61.0 | 30.38 | 12.32 | 27.0 | 3.55 | 0.84 | 0.95 | 22 |
| 4 | AP31 | Anvil Points | 30.6 | 19.63 | 20.55 | 14.0 | 1.84 | -- | 0.43 | 10 |
| 5 | AP24 | Anvil Points | 22.4 | 15.60 | 17.48 | 10.8 | 1.62 | 0.63 | 0.41 | 27 |
| 6 | AP8 | Anvil Points | 8.1 | 9.95 | 21.44 | 4.1 | 0.57 | 0.23 | 0.12 | 13 |
| 7 | RI8008-76 | Co.Core #3[b] | 22.0 | 12.56 | 12.32 | 9.2 | 1.71 | 1.35 | 1.16 | 78 |
| 8 | USNOSR-638 | Naval Reserve-1 | 1.9 | 4.65 | 11.40 | 1.5 | 0.46 | 0.87 | 0.54 | 92 |
| 9 | L-1(9A/5) | Anvil Points | 25.0 | 15.64 | 17.12 | 11.0 | 1.56 | 0.69 | 0.47 | 35 |
| 10 | GK5 | Geokinetics,Ut. | 4.7 | 6.53 | 15.20 | 2.4 | 0.51 | -- | 0.20 | 67 |
| 11 | HD25 | Horse Draw, Co.[c] | 25.0 | 19.20 | 29.50 | 11.1 | 2.02 | 0.60 | 0.45 | 32 |

a) Fraction of inorg. N $= \dfrac{\%N-0.0276(Org.C)}{\%N}$ (see discussion)
b) Northern Piceance Creek Basin at $\sim$ 230m, dawsonite rich.
c) Multi Mineral Corp., 649m, nahcolite rich.

Table 2
Identification of the 10 strongest diffraction
lines of buddingtonite in standards and oil shale samples.

| I/Io | hkl | d(Å) | | | | |
|------|-----|------|------|------|------|------|
| | | ASTM 17-517 | SI | RI8008 No76 | USNOSR 638' | CONDOR[a] |
| 100 | 130 | 3.81 | 3.82 | 3.71 | 3.79 | 3.82 |
| 95 | 010 | 6.52 | 6.52 | 6.52 | 6.52 | 6.52 |
| 70 | 220 | 3.38 | 3.35[b] | 3.35[b] | 3.34[b] | 3.386 |
| 70 | 202 | 3.25 | 3.24 | 3.24 | 3.23 | 3.2226 |
| 65 | 101 | 4.33 | 4.50[b] | 4.50[b] | 4.48[b] | 4.33 |
| 60 | 040 | 3.26 | 3.24 | 3.24 | 3.29 | 3.260 |
| 40 | 140 | 3.01 | 3.02 | 3.02 | 3.00 | 3.013 |
| 35 | 011 | 5.91 | 5.92 | 5.92 | 5.90 | 5.92 |
| 35 | 211 | 3.98 | 3.98 | 3.95 | 3.96 | 3.98 |
| 35 | 002 | 3.31 | 3.35[b] | 3.35[b] | 3.34[b] | 3.320 |

[a] Ref. (12).
[b] Spacings probably influenced by contributions from strong quartz peaks at d=3.47 and 4.25Å.

separated from Australian (Condor) shale are also compared in Table 2. The SI sample contains a large percentage of quartz, and the Green River Oil Shale samples contain large fraction of quartz, dolomite, and some dawsonite.

Our first evidence that buddingtonite is thermally stable came from its identification sample RI 8008-76 that had been heated to about 500°C in a covered crucible for one hour. Little of the carbon residue had been oxidized, so that this treatment roughly approximated Fischer Assay heating. Figure 1 compares the diffraction patterns of the raw and heated oil shale. The buddingtonite peaks are the same. In contrast, the dawsonite peaks are missing, confirming that the sample was heated above 350°C. We have also found that buddingtonite releases nitric oxide (NO) during oxidation after being heated to 500°C in an inert gas (4). The amount of NO was not effected by duration of preheating within the range 3 to 10 min. which indicates that the rate of ammonium release at 500°C is slow. These observations are consistent with (12) who found the x-ray diffraction patterns of buddingtonite does not change below 500°C. They found, in addition, that ammonium is lost by heating to 650°C, that remnants of the feldspar structure remains even upon heating to 750°C and that buddingtonite was not reformed by heating in a $NH_4OH$ solution at 180°C.

Ammonium ion identification in oil shale by infrared spectroscopy

Buddingtonite has a characteristic band at 1430 cm$^{-1}$ which distinguishes it from other silicates. The IR spectrum of our SI reference sample of Buddingtonite (13) is shown in Figure 2. The large adsorption in the 900-1300 cm$^{-1}$ region is characteristic of the Si-O stretch. Bands in the 600-800 cm$^{-1}$ region can be due to hydrocarbons as well as silicates. The ammonium ion has another adsorption band in the 3000-3500 cm$^{-1}$ region, but it is strongly overlapped by water bands, making it less characteristic.

In Green River oil shale, the 1430 cm$^{-1}$ band is overlapped by CH bending modes and also from a bending mode in the carbonate ion. Thus, to identify the ammonium ion definitively, it is necessary to remove organic material and carbonate minerals. Figure 3 shows an IR spectrum of sample AP24 that has had carbonate minerals removed by acid leaching. One would not ordinarily suspect the presence of ammonium ion because of the CH bending mode at 1350 to 1410 cm$^{-1}$. However, when organic material is removed by low-temperature ashing (using procedures described in detail in the next section), the ammonium-ion band emerges clearly, although not to the same relative intensity as in the spectrum of the SI buddingtonite or in the spectrum of buddingtonite reported by Loughnan and Roberts (12).

Figure 4 shows IR spectra of samples AP8 and AP60 after HCl leaching and low-temperature ashing. Sample AP8 shows little adsorption and sample AP60 shows none, which agrees with data on nitrogen content discussed in the next section.

Isolation of inorganic N by low-temperature ashing

The occurrence of inorganic N in Green River oil shale is clear based on x-ray and infrared evidence presented thus far, but a quantitative method of analysis for inorganic N is needed. While both x-ray diffraction and infrared spectroscopy have been used for quantitative mineral analysis, all of the inorganic forms of N have not necessarily been identified. In this section, a low-temperature ashing technique is developed for determination of inorganic N.

The most important variables in low-temperature ashing of oil shale are time, particle size, sample-stirring frequency and plasma activity. We have found that using 1 torr of $O_2$ and a power of 250 watts removed oil shale organic matter.

The role of particle size on the effectiveness of low-temperature ashing is shown in Figure 5. Both samples came to constant weight within 35 hours of ashing. The weight loss of the finer sample was 13.2%, which is about equal to the weight loss upon Fischer assay (12.84%) but the coarser sample lost only 9.3%. The time necessary to come to constant weight was cut in half if carbonates were removed with HCl before ashing.

The relative loss of organic C, H, and N during low-temperature ashing of Anvil Points shale, sample L-1 (9A/5), is shown in Figure 6. It is unlikely that organic C could be oxidized without also oxidizing organic H and N, so residual content of H and N is probably due to mineral forms.

Since buddingtonite is the only specific N-bearing mineral that has been identified in oil shale, we used it to test whether or not low-temperature ashing affects mineral N content. Table 3 gives total N content for a fine-ground sample of SI buddingtonite before and after being ashed for 35 hours (sample #12). The measured value of N content depended on the type of analysis being used, but the fraction of N remaining was over 90% by either analytical technique. This agrees with the qualitative observation in the previous section that ammonium-ion, as detected in the infrared spectrum, is not affected by ashing.

Table 3 also lists N content for a variety of raw and retorted oil shales before and after low-temperature ashing. The retorted samples were prepared by a modified Fischer Assay technique (16). The fraction of N removed by ashing ranges from nearly none to all. As discussed in more detail in the next section, this implies that the relative organic and inorganic N contents of Colorado oil shale are highly variable. Acid leaching of raw or retorted shale does not seem to make a systematic change in the fraction of N remaining after ashing, and the variation is probably a reflection of uncertainty in N concentration measurements.

DISCUSSION

One would think that a determination of the relative amounts of organic and inorganic N could be made by comparing N in whole shale to that in organic concentrates. Three workers have reported composition of raw shale and also the composition of the organic concentrates from the same shales from which the fractional recovery of N can be calculated (5-7). This is summarized in Table 4 along with a shale sample analyzed at LLNL. Approximately all of the N in raw shale is recovered in organic concentrate. This evidence has caused most workers to assume that the inorganic N content of oil shale is minor. In addition, elemental analysis of the organic material isolated from sample AP60 by Kirkman Bey and Campbell at LLNL indicated that all of the nitrogen in that sample is organic.

However, the results of (11) suggest that is not safe to use these results to conclude that there is little inorganic N in Green River oil shale. Using replicate results from several independent laboratories, (11) found that the Kjeldahl technique (digestion of the sample in hot concentrated sulfuric acid) gives systematically lower N values for Colorado oil shale than the Dumas (combustion) method. This is consistent with the need for HF digestion for the determination of fixed or "nonexchangeable" ammonium in soil and rock samples (17). If only organic N is detected by normal Kjeldahl analysis, it would be logical for most of it to be recovered in the organic concentrates even if greater quantities of inorganic N were present. Moreover, the rich oil shale used at LLNL is uniquely low in organic N.

A second way to estimate the relative abundance of inorganic N in either raw or retorted shale is to plot total N content verses organic C content. If the concentration of inorganic N is independent of organic C content and organic

Table 3
Wt%N in Raw, Retorted, and Low Temperature
Ashed Samples On a Raw Shale Basis

| Sample # | Material | Wt% N | | | % of Raw Shale N Remaining After LTA (±10%) |
|---|---|---|---|---|---|
| | | Raw | Retorted | LTA[a] | |
| 1 | Ca37 | 0.72 | -- | 0.17 | 24 |
| 1 | Ca37 | 0.72 | 0.35 | 0.15 | 21 |
| 2 | Ca25 | 0.58 | -- | 0.25[b] | 43[c] |
| 2 | Ca25 | 0.47 | -- | 0.31 | 66 |
| 2 | Ca25 | 0.58 | 0.43 | 0.33[b] | 57[c] |
| 2 | Ca25 | 0.47 | 0.49 | 0.20[b] | 42 |
| 3 | AP60 | 0.87 | -- | 0.01[b] | 1[c] |
| 3 | AP60 | 0.98 | -- | 0.09[b] | 9 |
| 3 | AP60 | 0.87 | 0.28 | 0.02[b] | 2[b] |
| 3 | AP60 | 0.98 | 0.45 | 0.06[b] | 6 |
| 4 | AP31 | 0.47 | -- | 0.11 | 23 |
| 4 | AP31 | 0.47 | 0.27 | 0.11 | 23 |
| 5 | AP24 | 0.39 | -- | 0.14 | 36 |
| 6 | AP8 | 0.09 | -- | 0.02 | 22 |
| 7 | RI8008-76 | 1.13 | -- | 0.72[b] | 64 |
| 8 | USNOSR-638 | 0.55 | -- | 0.56[b] | 102[c] |
| 8 | USNOSR-638 | 0.49 | -- | 0.43[b] | 88 |
| 9 | L-19A/5 | 0.47 | -- | 0.28[b] | 59 |
| 10 | GK5 | 0.32 | -- | 0.28 | 56 |
| 10 | GK5 | 0.32 | 0.22 | 0.19[b] | 59 |
| 11 | HD25 | 0.52 | -- | 0.21 | 56 |
| 11 | HD25 | 0.52 | 0.26 | 0.25 | 48 |
| 12 | Buddingtonite | 1.69 | -- | 1.80[b] | 107 |
| 12 | Buddingtonite | 2.78 | -- | 2.58[b] | 93[c] |

(a) LTA of retorted shale if preceeded in table by retorted shale data, otherwise the LTA was done on raw shale.
(b) Acid leached (HCℓ) to accelerate ashing
(c) Chemical Analysis by J and A Associates, Inc. Golden, CO

Table 4
Comparison of N/org.C mole ratios for raw shale and organic
concentrates from the same shales

| N/Org.C Mole Ratio | | Recovered | Reference |
|---|---|---|---|
| Raw Shale | Org. Concentrate | %N | |
| 0.029 (a) | 0.032 | 110% | (7) |
| 0.027 (b) | 0.025 | 93% | (6) |
| 0.033 (c) | 0.029 | 88% | (5) |
| 0.029 (d) | 0.016 | 89% | (5) |
| 0.032 (e) | 0.033 | 103% | LLNL |

(a) Average of 9 samples, mineable beds, mahogany ledge (Anvil Points).
(b) Ten samples from the mahogany zone, 25 gpt.
(c) One sample, mahogany zone.
(d) One sample "papery" shale.
(e) One sample AP60, work done at LLNL.

Table 5
Nitrogen-organic carbon correlation

Data fit to expression: Wt%N=a+b(Wt% org. carbon)
Wt% N=total nitrogen content of sample
a=Wt% inorg. nitrogen
b=Wt ratio org. nitrogen/org. carbon

Raw Shale

| a | b | Samples | Sample Type and Location | Reference |
|---|---|---|---|---|
| 0.225 | 0.0275 | 260 | 2 core holes, USNOSR | (8) |
| 0.096 | 0.0286 | 66 | Colorado and Utah | (9) |
| -0.020 | 0.0320 | 40 | 1 core Utah, Geokinetics | LLNL Analyses |
| 0.10 | 0.0249 | 6 | 1 sample split, Colony (Ca) | (18) |
| 0.036 | 0.0307 | 9 | Mineable beds, Anvil Points | (17) |
| 0.252 | 0.015 | 6 | Selected samples, Anvil Points | (7) |
| 0.046 | 0.0318 | 58 | Core KEP No 5, Kentucky | (18) |
| 0.012 | 0.031 | 34 | T16 Core, Kentucky | (19) |

Retorted Shale

| a | b | Samples | Sample Type and Location | Reference |
|---|---|---|---|---|
| 0.042 | 0.0665 | 66 | Colorado and Utah | (9) |
| -0.009 | 0.069 | 9 | "mineable" beds, AP | (7) |
| 0.045 | 0.035 | 18 | from NTU Retort[a] | (20) |

[a] Some samples only partly retorted, some samples oxidized.

material has a constant N/C ratio, the slope of the plot gives the ratio of organic N to organic C, and the intercept gives the concentration of inorganic N. The observation that N content of oil is independent of grade (9) supports our assumption of constant kerogen composition. The results of linear regression analysis of several sets of data in the literature are given in Table 5, including data from two Kentucky oil shale cores, and some data for retorted shales.

A positive intercept is found for each set of samples except for those from the Geokinetics core from Utah which has a negative intercept of -0.020. The organic N to organic C wt ratio for Green River oil shales is 0.0276 which is a value calculated from the slopes in Table 4 weighted in proportion to the number of samples. The value of this ratio for retorted shale is 0.064.

A comparison of the fraction of inorganic N determined by the two methods for 11 shale samples is given in Fig. 7. Although a trend is clear considerable differences stand out for some samples.

The correlation coefficient for the linear regression analysis of N/org. C for the data of Giauque et al. (8) is 0.79. We feel that the observed random variation in N content (above a minimum value) for a given organic C content is due mostly to a variation in the inorganic N content.

With respect to the fates of organic and inorganic N during pyrolysis, we have shown that buddingtonite is relatively stable in the absence of air at temperatures up to 500°C and that inorganic N is not generally lost during retorting of shales, but the uncertainty is large due in part to the lack of accuracy in measuring N content in samples with low N concentrations.

CONCLUSIONS

On the average, approximately half of the N in the Green River Formation is inorganic, but the distribution is not uniform. Inorganic N in raw shale tends to remain in the shale after retorting. Buddingtonite, an ammonium feldspar, has been identified by means of x-ray diffraction in some oil shale samples. Ammonium ions have been identified in the same and other samples by means of infrared adsorption. Low-temperature ashing of oil shale by means of an oxygen plasma has been found to remove organic N, but not inorganic N in buddingtonite. Measurement of total N after low-temperature ashing is proposed as a way of determining inorganic N content. Due in part to the difficulty of measuring N concentration is samples with little N the method is qualitative. A second method for the estimation of the inorganic N content of shale is based on the assumption that the org. N/org.C ratio is constant. At present it is not clear if one estimate is better that the other.

In view of the present results, the stoichiometry of retorting must be revised. Organic material in raw shale and in the char in retorted shale contains less N than previously thought. The CH&N composition of organic material in raw shale should be represented by the formula $CH_{1.50} N_{0.024}$. The chemical composition of organic material in retorted shale should be represented by the formula $CH_{0.42} N_{0.06}$.

## Acknowledgment

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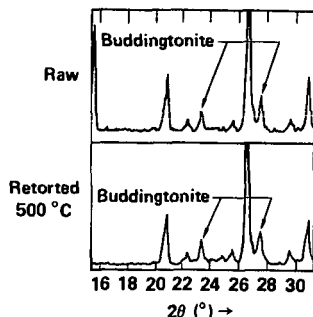
Figure 1.  X-ray diffraction pattern of raw and retorted oil shale sample RI 8008-76 in which buddingtonite is found.  Retorting does not eliminate the lines due to buddingtonite.  The large peak on the left side of the raw-shale pattern is due to dawsonite.  This mineral is decomposed during retorting.
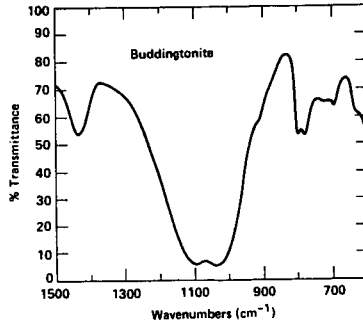
Figure 2. Infrared adsorption of buddingtonite showing the 1430 cm$^{-1}$ peak due to ammonium ions. Sample from the Smithsonian Institute (SI), White (13).
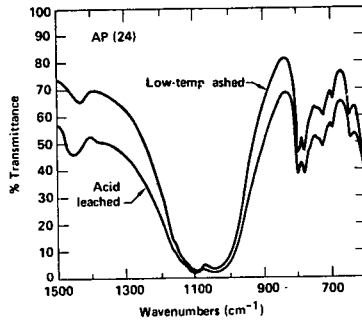


Figure 3. Change of infrared adsorption AP(24) shale. Lower curve acid leached shale and upper curve acid leached and low-temp ashed.
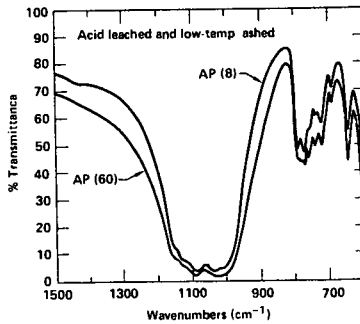


Figure 4. Infrared absorption of shales AP(60) and AP(8) which have been acid leached and low-temperature ashed. Shale AP(8) shows some ammonium-ion absorption and shale AP(60) does not.
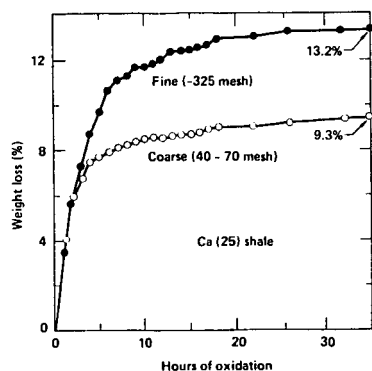
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Figure 5. Weight loss during low-temperature ashing of raw shale Ca(25). The samples were stirred at the time of each data point.
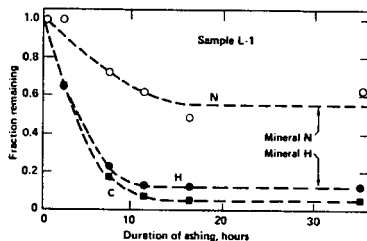


Figure 6. Fractional loss of N, H, and C during low-temperature ashing of sample L-1(9A/5). Residual N and H is due to the presence of these elements in minerals.
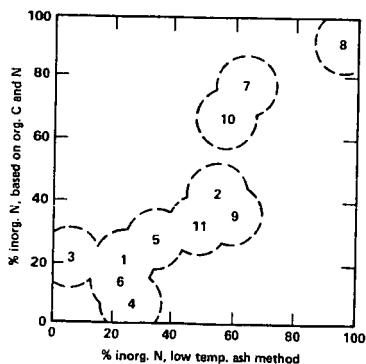


Figure 7. Comparison of inorg. N content of 11 shale samples as determined by two methods.

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